

Processes Involving Excited Atoms in Gas Discharge Plasma of Inert Gases

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ABSTRACT: Processes are considered in a uniform gas discharge plasma which include elastic and inelastic collisions of electrons with atoms. The rate constants of excitation and quenching processes with transition between s and p states of a valence electron are evaluated on the basis of experimental data for alkali metal atoms. The atom excitation process in a gas discharge plasma of inert gases has a self-consistent character, so that the excitation process leads to a decrease of the energy distribution function of electrons with an increasing energy under the action of the excitation process, that in turn leads to a decrease of the excitation rate constant. As a result, the energy distribution function of electrons in a gas discharge plasma drops sharply with an increasing electron energy above the threshold of atom excitation, and therefore the population of higher excited states is lower significantly than that for lower excited states. Hence, stepwise ionization proceeds through the lowest excitation states. The concentration of excited atoms and the rate of atom stepwise ionization in a gas discharge plasma of inert gases are evaluated. It is shown that many regimes of equilibrium in this plasma may be realized depending on its parameters that makes an universal method of numerical analysis of this plasma to be unpractical. In additions, cross sections and rate constants of processes in a gas discharge plasma require a careful grounding, especially, for electron-atom collisions.

1. INTRODUCTION

A gas discharge plasma is a weakly ionized gas which is formed and is supported under the action of an external electric field. Usually a gas discharge plasma is a nonequilibrium system, where formation of new charged particles, electrons and ions, results from electron-atom collisions. Therefore properties of a gas discharge plasma are determined by processes inside it, and there are various regimes of a gas discharge plasma depending on basic processes [1, 2, 3]. We are guided below by a gas discharge plasma of inert gases. Though the processes involving molecular particles and negative ions are excluded in this cases, many regimes may be realized depending on external conditions and plasma parameters. These possibilities are represented in Table 1 [3]. We below consider only cases when excited atoms are of importance for plasma properties. In particular, the presence of excited atoms in a gas discharge plasma can lead to the stepwise character of atom ionization in collisions of electrons with atoms.

Table 1 Factors which determine corresponding regimes of a gas discharge plasma.

	Factor	Possibilities
1.	Energy distribution function for thermal electrons	The electron distribution function may be determined by electron-atom collisions or electron-electron collisions depending on the number density of electrons
2.	Single or stepwise ionization	Depending on the number density of electrons, the ionization process of gas atoms by electron impact results from single ionization of atoms in the ground state or proceeds through excited states

3.	Radiative transitions between atom states	Excited atoms are quenched in collisions with electrons or as a result of photon emission
4.	Atomic or molecular ions in a plasma	The rate of plasma decay proceeds through different processes depending on an ion sort
5.	Ionization through excited atom states	Associative ionization or Penning process may influence on plasma parameters
6.	Heat processes	Diffusive and constricted forms of the positive column
7.	Cathode processes	Emission electrons from the cathode may proceed by cathode bombardment by ion impact or thermoemission

Restricting ourselves by processes with formation and participation of excited atoms in a gas discharge plasma, we take into account the following properties of this plasma. Usually the electric field strength is respectively small, so that the average electron energy is small compared to the excitation energy. Therefore excitation of atoms corresponds to the tail of the energy electron distribution function (EEDF). Then atom excitation in a gas discharge plasma has a self-consistent character [4, 5] as it is demonstrated in Fig. 1. Indeed, the excitation process corresponds to energies above the excitation threshold where EEDF falls sharply due to this process. In turn, for the same reason, this process leads to a decrease of the effective excitation rate. From Fig. 1 it follows that at higher energies the presence of excited atoms leads to a recovery of EEDF due to quenching of excited atoms in collisions with slow electrons. According to this character of atom excitation, this process results from electron diffusion in an energy space for electron energies below the atom excitation energy and by the cross section of atom excitation by electron impact if its energy exceeds the atom excitation energy. In this paper we analyze these processes on the basis of analytic methods. In this analysis we do not oppose the analytic methods in the analysis of a gas discharge plasma to numerical ones. Indeed, a gas discharge plasma is a complex physical object, and its detailed analysis requires computer methods. But for reliable numerical evaluations of parameters of a certain gas discharge plasma it is necessary to understand its nature. Therefore the analytical analysis of process in a gas discharge plasma and its kinetics helps to its reliable modeling on the basis of numerical methods.

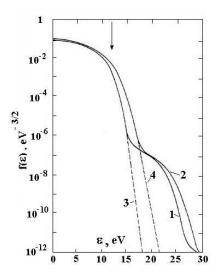


Figure 1: EEDF in argon at the electric field strengths of 10 Td (curves 1 and 3) and 20 Td (curves 2 and 4) under stationary conditions according to calculations [5]. In the case of curves 1 and 2 the concentration of metastable argon atoms is $c_m = 6.10^{-5}$), and in the case of curves 3 and 4 metastable atoms are absent in ionized argon. The arrow indicates the excitation energy of the metastable state

2. KINETICS OF FORMATION OF EXCITED ATOMS IN GAS DISCHARGE PLASMA

2.1 Elementary Processes in Electron-atom Collisions

Elementary processes determine kinetics and properties of a gas discharge plasma. In the case of a plasma of inert gases they include in the first place elastic and inelastic electron-atom collisions. The problem in the analysis of these processes is such that theory does not allows to evaluate the cross sections of electron-atom collisions reliable at not large electron energies. Indeed, the collision theory involving electrons (for example, [6, 7]) has not such methods as the density functional theory which gives the possibility to account for exchange interactions between an incident and bound electrons. Often experiments give scanty information about parameters of collision processes involving slow electrons. Nevertheless, the theory gives some precise relations and useful models for cross sections of electron-atom collisions, and we consider them below.

As for electric collisions between electrons and atoms of inert gases, the results of measurements for cross sections of these processes are summed in [8], and we use this. In the analysis of inelastic electron-atom collisions, we analyze in the first place the processes of excitation of the ground atom state and quenching of an excited atom state by electron impact. One can connect the cross section of atom excitation by electron impact σ_{ex} and the cross section σ_q of the inverse process - atom quenching by electron impact on the basis of the principle of detailed balance. We below represent the principle between the process of atom excitation be electron impact and the inverse process, quenching of an excited atom in collisions with electrons. These processes are described by the scheme

$$e(\varepsilon) + A_o \leftrightarrow e(\varepsilon - \Delta \varepsilon) + A_*$$
 (2.1)

Here the argument indicates the electron energy, A_0 , A_* is the atom notation in the ground and excited states respectively, $\Delta \varepsilon$ is the excitation energy.

Following to [10], we introduce the interaction operator V between colliding electron and atom, and this interaction causes the transition between the ground o and excited * states. Considering this interaction as a perturbation, we have for the excitation probability per unit time [9]

$$P_{o^*} = \frac{2\pi}{\hbar} |V_{o^*}|^2 \frac{dg_*}{d\varepsilon} = \frac{v_o \sigma_{ex}}{\Omega}, \qquad (2.2)$$

where V_{o*} is the matrix element between the transition states, $dg_*/d\varepsilon$ is the statistical weight of the excited state per unit of energy, v_o is the initial electron velocity. In considering this equilibrium, we assume that one electron and one atom are located in a volume Ω . Because the operation of time reversal corresponds to a change $Vo_* \to V_{*o}^*$, we obtain the following relation [10]

$$v_{o} \frac{dg_{o}}{d\varepsilon} \sigma_{ex}(\varepsilon) = v_{*} \frac{dg_{*}}{d\varepsilon} \sigma_{q}(\varepsilon - \Delta\varepsilon), \tag{2.3}$$

where g_o , g_* are the statistical weights for the electron-atom system in the ground and excited atom states correspondingly, the argument indicates an energy at which the cross section is taken.

The statistical weight of the electron and atom in the ground state is given by

$$dg_o = g_o \cdot 2\Omega \frac{d\mathbf{p}_o}{(2\pi\hbar)^3},\tag{2.4}$$

where g_o is the statistical weight of the atom ground state, the factor 2 accounts for the electron spin states. The analogous expression respects to the statistical weigh of the electron-atom system with the atom in the excited state. As a result, formula (2.3) gives

$$g_{o}\varepsilon\sigma_{ex}(\varepsilon) = g_{*}(\varepsilon - \Delta\varepsilon)\sigma_{o}(\varepsilon - \Delta\varepsilon)$$
(2.5)

Introducing the rate constant of atom excitation by electron impact $k_{ex}(\varepsilon)$ as

$$k_{ex}(\varepsilon) = \sqrt{\frac{2\varepsilon}{m_e}} \sigma_{ex}(\varepsilon),$$
 (2.6)

where m_e is the electron mass. Correspondingly, the principle of detailed balance leads to the following relation between the rate constants of atom excitation $k_{ex}(\varepsilon)$ and quenching $k_a(\varepsilon - \Delta \varepsilon)$ by electron impact

$$k_{ex}(\varepsilon) = k_q(\varepsilon - \Delta \varepsilon) \frac{g_*}{g_o} \sqrt{\frac{\varepsilon - \Delta \varepsilon}{\varepsilon}}, \qquad (2.7)$$

where ε is the energy of an incident electron, g_o , g_* are the atom statistical weights for the ground and excited states.

One more precise relation for parameters of electron-atom collisions is the threshold law for the excitation cross section σ_{ex} of an atom by electron impact that has the form [11, 6]

$$\sigma_{ex}(\varepsilon) \sim \sqrt{\varepsilon - \Delta \varepsilon}$$
 (2.8)

From this on the basis of the principle of detailed balance one can find that the quenching rate constant is independent of the electron energy at low energies. In particular, one can use the Maxwell distribution function of electrons over energies $f(\varepsilon)$ at the electron temperature T_{ε} that has the form

$$f(\varepsilon) = N_e \sqrt{\frac{2}{\pi}} \frac{\varepsilon^{1/2}}{T_e^{3/2}} \exp(-\varepsilon / T_e), \qquad (2.9)$$

where N_e is the electron number density.

Introducing the average rate constant of atom excitation by electron impact $\overline{k_{ex}}$ as

$$\overline{k_{ex}} = \frac{1}{N_c} \int k_{ex} f(\varepsilon) d\varepsilon, \qquad (2.10)$$

where the energy distribution function of electrons is normalized by the relation

$$\int f(\varepsilon)d\varepsilon = N_e \tag{2.11}$$

In particular, in the case of the Maxwell distribution function the principle of detailed balance leads to the following relation between the average rate constants of excitation $\overline{k_{ex}}$ and quenching $\overline{k_q}$

$$k_{th} = \overline{k_{ex}} = \overline{k_q} \frac{g_*}{g_o} \exp\left(-\frac{\Delta \varepsilon}{T_e}\right), \tag{2.12}$$

This rate constant corresponds to the thermodynamic equilibrium for the ground and excited atom states and electrons.

These relations may be used for practical values of the parameters of inelastic electron-atom collisions together with some theoretical models [12, 13, 14] and measured data. Among various theoretical models we choose below

the model [15, 16] which continues the Born approximation at large collisions energies to low energies. At large collision energies the cross section of atom excitation by electron impact is proportional to the square of the atom dipole moment operator D_{o^*} . This means that effective excitation of atoms by electron impact takes place only for atom resonant states which are connected with the ground atom state by a dipole radiative transition. Hence within the framework of this model one can find that the excitation cross section is inversely proportional to the radiative time τ_r for the radiative transition between excited and ground states. From this it follows a certain scaling law which gives for the rate constant. In particular, at low electron energies in the case of atom quenching and near the threshold of atom excitation this model gives [17, 18]

$$k_{q} = \frac{k_{o}}{(\Delta \varepsilon)^{7/2} \tau_{r}}, k_{ex} = \frac{k_{o} g_{*}}{g_{o} (\Delta \varepsilon)^{7/2} \tau_{r}} \sqrt{\frac{\varepsilon - \Delta \varepsilon}{\varepsilon}}$$
(2.13)

with the numerical parameter k_a which follows from experimental data.

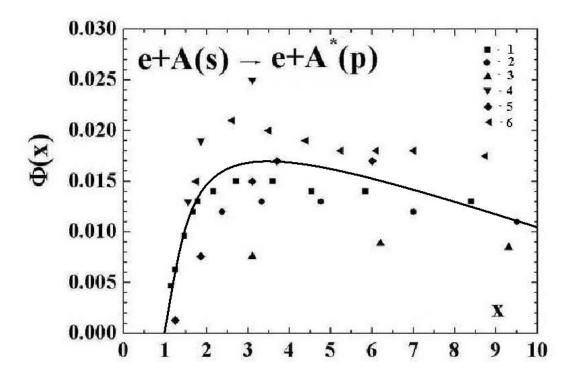


Figure 2: Dependence on the reduced electron energy ε/Δ ε for the reduced cross section of excitation Φ according to formula [3]. These data are based on atom resonant excitation by electron impact from the ground states of lithium, sodium and potassium atoms and from the metastable states $He(2^3 S)$ for the helium atoms with using the following experimental data: 1 - [19] for Li, 2 - [20] for Na, 3 - [21] for K, 4 - [22] for K, 5 - [23] for K, 6 - [24, 25] for $He(2^3 S)$.

Let us reduce experimental data to this concept. To demonstrate this, we give in Fig. 2 [3] the reduced cross section in the case of the s-p transition of a valence electron on the basis of cross sections of excitation of alkali metal atoms by electron impact. In this case we represent the excitation cross section in the form

$$\sigma_{0*} = \sigma_* \Phi\left(\frac{\varepsilon}{\Delta \varepsilon}\right), \sigma_* = \frac{2\pi e^4}{\Delta \varepsilon^2} f_{o^*},$$
 (2.14)

where f_{o^*} is the oscillator force for transition between s and p states which is averaged over states of the group o and is summed over states of the group o. In the limit of small x - I we have

$$\Phi(x) = a\sqrt{x-1}, x \to 1, \tag{2.15}$$

where $a = 0.130 \pm 0.07$ [18]. Note that the dispersion of data of Fig. 2 in a greater extent is connected with the accuracy of measurements. One can be convinced in this by comparison for excitation cross section of a potassium atom by electron impact in Fig. 2. In addition, experimental data for excitation cross sections of alkali metal atoms by electron impact allow us to find the parameter k_o in formula. Using experimental data [13, 26, 27, 23] for excitation of potassium, rubidium and cesium atoms by electron impact from the ground state to the states K (4² P), Rb(5² P), Cs(6² P), we find $k_o = (4.3 \pm 0.7)$. 10^{-5} cm^3/s [17, 18] for \$s-p\$s-p electron transition, and accuracy of this value, as well as the reduced cross section of Fig. 2, is estimated also as 20-30%. In this case the quenching rate constant in the limit of low electron energies is given by

$$k_q = const \frac{g_o f_{0*}}{g_* (\Delta \varepsilon)^{3/2}} = \frac{k_o}{(\Delta \varepsilon)^{7/2} \tau_r}$$
 (2.16)

2.2 Electron Drift in Energy Space Below Atom Excitation Energy

One can analyze the character of electron evolution in a gas discharge plasma on the basis of the kinetic equation for the electron distribution function that may be expanded over spherical harmonics [28, 29, 30, 31, 32, 34, 35]

$$f(\mathbf{v}) = f_0(v) + v_x f_1(v), \tag{2.17}$$

where *x* is the direction of an electric field. From the kinetic equation we have for the spherically symmetric part of the distribution function

$$\frac{\partial f_0}{\partial t} - \frac{a^2}{3v^2} \frac{d}{dv} \left(\frac{v^2}{v_{ea}} \frac{df_0}{dv} \right) = I_{ea}(f_0) + I_{ee}(f_0) - N_a \int_{\Delta \varepsilon}^{\infty} k_{ex}(\varepsilon) f_0(\varepsilon) d\varepsilon + N_* \int_0^{\infty} k_q(\varepsilon - \Delta \varepsilon) f_0(\varepsilon - \Delta \varepsilon) d\varepsilon - \frac{f_0(\varepsilon)}{\tau},$$
(2.18)

Here f_0 is the spherically symmetric part of the electron distribution function, $a = eE/M_e$, where E is the electric field strength, m_e is the electron mass, v is the electron velocity, $v_{ea} = N_a v \sigma_{ea}^*(v)$ is the rate of elastic collisions of electrons with atoms, so that N_a is the number density of atoms, and $\sigma_{ea}^*(v)$ is the diffusion cross section of electronatom scattering, I_{ea} (f_0) and I_{ee} (f_0) are the collision integral for the spherical part of the distribution function for electron collisions with atoms and electrons correspondingly, N_* is the number density of excited atoms, τ is a relaxation time. It is supposed in equation that plasma parameters are independent of a space. In addition, because of small energy variation in electron-atom collisions [35], the electron-atom collision integral I_{ea} (f_0) may be represented as a diffusion flux in an electron energy space [10, 34]. The same relates to the electron-electron collision integral I_{ee} (f_0) [36] because the basic contribution to the diffusion cross section of electron-electron scattering follows from scattering at small angles, but the flux is a bilinear function of the distribution function. Because for excitation processes electrons are divided in thermal and fast ones and fast electrons are responsible for atom excitation, the electron-electron collision integral I_{ee} (f_0) may be represented as a diffusion flux for the distribution function in an electron energy space, as well as the electron-atom collision integral I_{ea} (f_0). Let us consider the excitation process as motion of a test electron in a space of electron energies. If the excitation process proceeds fast as the electron energy reaches the atom excitation energy, diffusion of a test electron in an energy spacedetermines the excitation rate [55].

This equation allows one to analyze the character of variation of the electron distribution function on the basis of the kinetic equation. Indeed, one can separate the energy ranges of Fig. 1 in four parts. In the first range below the excitation energy $\varepsilon < \Delta \varepsilon$ equation takes the form

$$\frac{\partial f_0}{\partial t} - \frac{a^2}{3v^2} \frac{d}{dv} \left(\frac{v^2}{v_{ea}} \frac{df_0}{dv} \right) = I_{ea}(f_0) + I_{ee}(f_0)$$
(2.19)

In the second range above the excitation threshold a sharp decrease of the EEDF proceeds because of the excitation process. In the third range with a more weak drop of the EEDF the quenching process involving excited atoms is responsible for formation of fast electrons. In the last range with a sharp drop of the EEDF other inelastic processes including atom ionization become essential in the establishment of the EEDF.

Let us analyze the character of atom excitation by electron impact in a gas discharge plasma at low electric field strength where the average electron energy $\bar{\varepsilon}$ is small compared to the atom excitation energy $\Delta \varepsilon$. Then a slow electron acquires a sufficient energy for atom excitation as a result of many collisions. In this case the process of atom excitation by electron impact is realized as a result of many electron-atom collisions. Under these conditions it is convenient to define the effective rate constant of atom excitation k_{ε} as

$$\frac{dN_*}{dt} = N_a k_{<} \tag{2.20}$$

Here N_* is the number density of excited atoms, and $N_* \ll N_a$, where N_a is the number density of atoms in the ground state. This equation follows from the kinetic equation by it integration over electron energies. Evidently, this rate constant is proportional to the electron diffusion coefficient in a space of electron energies. Indeed, we have in this case [3]

$$k_{<} = \frac{4\pi v_o (B_E + B_{ea} + B_{ee})}{m_e N_o} \frac{d\varphi_0(\varepsilon)}{N_o d\varepsilon} \Big|_{\varepsilon = \Delta \varepsilon}, \tag{2.21}$$

where $v_o = \sqrt{2\Delta\varepsilon/m_e}$ is the electron velocity at the excitation threshold, and the distribution function $\varphi_0(\varepsilon)$ does not take into account the loss of fast electrons as a result of atom excitation. The electron diffusion coefficients of formula in the energy space due to electric field B_E , electron-atom collisions B_{ea} and electron-electron collisions B_{ee} are equal

$$B_{E} = \frac{m_{e}a^{2}v_{o}^{2}}{3v_{ea}}, B_{ea}(\varepsilon) = \frac{m_{e}}{M}Tm_{e}v^{2}v_{ea}, B_{ee}(\varepsilon) = \frac{4\pi e^{4}T_{e}}{m_{e}v}N_{e}\ln\Lambda$$
(2.22)

Here T is the gas temperature, is the electron velocity, $\ln \Lambda$ is the Coulomb logarithm, and the diffusion coefficient of electrons B_{ee} is given for the regime of a high electron number density, where the electron temperature may be introduced. It should be noted also that though mechanisms of energy transfer may be different depending on the character of variation of the electron momentum.

2.3 EEDF at Energies Above Excitation Threshold

We now analyze the EEDF at electron energies above the excitation threshold where the atom excitation process by electron impact proceeds along with elastic electron-atom collisions. Above in considering the excitation process in a gas discharge plasma at low electric field strengths we used the model [3] where atom excitation takes place if an electron energy reaches the atom excitation energy. In this case the excitation cross section is large, so that each electron whose energy exceeds the atom excitation energy excites an atom, rather than returns below the excitation

threshold as a result of elastic collisions. Next, the rate of atom excitation is determined by the electron flux in the direction of large electron energies under the action of an external electric field, and this flux is compensated by atom excitation that makes fast electrons to be slow ones.

We now consider in detail the behavior of the EEDF above the excitation threshold where it falls sharply with an increasing energy. This is a self-consistent process which connects the atom excitation rate due to collisions with electrons and variation of the EEDF with an electron energy increasing. A sharp variation of the EEDF with an increasing energy allows one to use the the quasiclassical method for the distribution function representing it near the excitation threshold in the form

$$f(v) = f(v_o) \exp(-S),$$
 (2.23)

and the condition of a sharp fall of the EEDF with an increasing electron energy above the excitation threshold is

$$(S')^2 \gg S" \tag{2.24}$$

It is convenient to use the electron velocity v as an argument of the distribution function, and $v_o = \sqrt{2\varepsilon/m_e}$. Under these conditions the exponent is given by [37, 18]

$$S = \frac{2g_*}{3g_o} \frac{\sqrt{3v_{ea}v_{ex}}}{a} \left(\frac{(v - v_o)}{v_o}\right)^{3/2},$$
(2.25)

where $v_{ea} = N_a v \sigma_{ea}^*$ is the rate of elastic electron-atom scattering, $v_{ex} = N_a k_{ex}$ is the rate of atom excitation, and variation of the electron momentum results from elastic electron-atom collisions, that is

$$v_{ea} \gg v_{ex} \tag{2.26}$$

In the case where the quasiclassical solution holds true, it is convenient represent expression in the form [37, 18]

$$S = \frac{2v_o}{5a} \sqrt{3 \frac{g_*}{g_o}} v_q v_o \left(\frac{\varepsilon - \Delta \varepsilon}{\Delta \varepsilon} \right)^{5/4}$$
 (2.27)

Here we use the rate of elastic electron-atom collisions at the excitation threshold $v_o = v(v_o)$, and the rate of quenching of an excited atom by slow electrons $v_q = N_a k_q$, because the rate constant of quenching of the excited atom by a slow electron k_q is independent of the electron energy. Next, $a = eE/m_e$ with E- the electric field strength, g_o , g_* are the statistical weights of the ground and excited atom states. Thus near the excitation threshold we have according to formula

$$S = \kappa \left(\frac{\varepsilon - \Delta \varepsilon}{\Delta \varepsilon}\right)^{5/4},\tag{2.28}$$

where

$$\kappa = \frac{2v_o}{5a} \sqrt{3\frac{g_*}{g_o} v_q v_o},\tag{2.29}$$

and the condition that the EEDF falls sharply with an increasing electron energy above the excitation threshold is

$$\kappa \gg 1$$
 (2.30)

These formulas allow us to determine the rate of atom excitation by electron impact under the assumption that this process proceeds near the excitation threshold. We have for the excitation rate

$$\frac{dN_*}{dt} = N_a \int k_{ex} f_0(v) \cdot 4\pi v^2 dv, \qquad (2.31)$$

if the distribution function is normalized by the condition

$$\int f_0(v) \cdot 4\pi v^2 dv = N_e \tag{2.32}$$

Using the principle of detailed equilibrium, we have

$$\frac{dN_*}{dt} = \frac{4\pi v_o g_*}{m_e g_o} v_q f_0(v_o) \int_{\Delta \varepsilon}^{\infty} \sqrt{\frac{\varepsilon - \Delta \varepsilon}{\Delta \varepsilon}} e^{-s} d\varepsilon, \qquad (2.33)$$

where $v_q = N_a k_{q'}$ is the rate of quenching of an excited atom by a slow electron. It is convenient to introduce the rate constant of atom excitation as

$$k_{>} = \frac{1}{N_{a}N_{e}} \frac{dN_{*}}{dt},$$
 (2.34)

and from this it follows $k \sim \kappa^{-1.6}$.

Since the parameter κ is inversely proportional to the electric field strength $\kappa \sim 1/E$ (precisely, to the reduced electric field strength E/N_a), this regime with a sharp decrease of the EEDF above the excitation threshold takes place at low electric field strength. Since we consider excitation processes in inert gases, we give in Table 2 values of the parameter κ and accompanied parameters for excitation of atoms of heavy inert gases by electron impact. We take the elastic cross section at the threshold from [8], the cross sections of quenching of the state 3P_2 from [38], and the same rate constant we take for the state 3P_0 , and the quenching rate constants for the states 3P_1 , 1P_1 are calculated on the basis of formula.

Table 2
Parameters of excitation of helium and argon atoms in a gas discharge plasma.

Atom	$Ar(^3P_2)$	$Ar(^3P_1)$	$Ar(^{3}P_{0})$	$Ar(^{1}P_{0})$
$\Delta \varepsilon$, eV	11.55	11.62	11.72	11.83
k_q , $10^{-9} cm^3/s$	0.4	0.82	0.4	3.9
κ	65	34	30	136
Atom	$Ne(^3P_2)$	$Ne(^{3}P_{1})$	$Ne(^{3}P_{0})$	$Ne(^{1}P_{0})$
$\Delta \varepsilon$, eV	16.61	16.67	16.71	16.84
k_q , $10^{-9} cm^3/s$	0.2	0.09	0.2	1.4
κ	65	34	30	136
Atom	$Kr(^3P_2)$	$Kr(^3P_1)$	$Kr(^3P_0)$	$Kr(^{1}P_{0})$
$\Delta \varepsilon$, eV	9.915	10.032	10.562	10.644
k_q , $10^{-9} cm^3/s$	0.3	3.1	0.3	2.4
*				

κ	135	320	63	290
Atom	$Xe(^3P_2)$	$Xe(^{3}P_{1})$	$Xe(^3P_0)$	$Xe(^{1}P_{0})$
$\Delta \varepsilon$, eV	8.32	8.44	9.45	9.57
k_q , $10^{-9} \text{ cm}^3/\text{s}$	1.9	6.8	1.9	6.8
κ	361	535	178	478

To sum up for atom excitation in a gas discharge plasma by electron impact, we have at low electric field strengths two ranges in an electron energy space which are responsible for this process, namely, the range below the atom excitation energy, where the electron flux to the excitation energy is supported by an external electric field, and the range the atom excitation energy, where the excitation process proceeds in a narrow energy range. One can sew the rates of these processes in the total excitation process, and the total excitation rate constant of atom excitation by electron impact k_{ex} in a gas discharge plasma is summed from the rate constants of these processes as [39, 3]

$$k_{\rm ex} = \frac{k_{\rm s}k_{\rm s}}{k_{\rm s} + k_{\rm s}} \tag{2.35}$$

2.4 Principles of Equilibrium in Gas Discharge Plasma

In this consideration we simplify the problem of a gas discharge plasma restricting ourselves by processes of elastic electron-atom collisions and also by processes of excitation of atoms in a ground state and quenching of atoms in excited states in collisions with electrons. One can expect that in this simple case one can describe regimes of existence of a gas discharge plasma in a universal method. We discuss below the character of processes in this case.

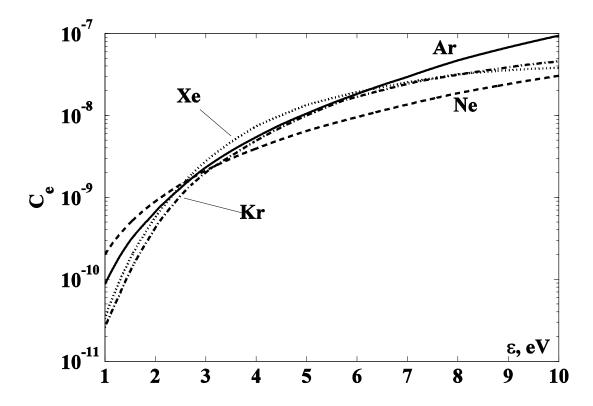


Figure 3: Transition between the regimes of low and high electron concentration on the basis of the relation $B_{ee} = B_{ea}$).

In this case we have several parameters which determine the character of atom excitation, and they include the electron concentration $c_e = N_e/N_a$, the reduced electric field strength E/N_a , and the number density of atoms N_a . It should be noted that the regimes of low and high electron concentrations (Table 1) lead to different form of the EEDF in the energy range below the atom excitation energy. For definiteness, we consider the regime of a high electron concentration, where the electron temperature may be introduced. This regime corresponds to the criterion in formula

$$B_{ea} \ll B_{ee}, \tag{2.36}$$

and we give in Fig. 3 the electron concentration for the boundary between these regimes depending on the electron energy ε for heavy inert gases. It should be noted that the diffusion coefficient B_{ee} due to electron-electron collisions in a space of electron energies ε corresponds to the criterion

$$\varepsilon >> T_{\rho}$$
 (2.37)

Indeed, this quantity follows from the Landau collision integral [36] that is a bilinear functional from the electron distribution function over electron velocities (or energies). To transform the collision integral into a linear functional, we divide electrons in thermal and fast ones. Thermal electrons are characterized by the Maxwell distribution function with the electron temperature T_e , and fast electrons determine excitation of atoms. For definiteness, we take in Fig. 3 the electron temperature $T_e = 2eV$.

One can add to this that in reality the electron temperature is not small for the regime under consideration where a gas discharge plasma exists. One can expect a typical electron temperature is $T_e \sim \text{le} V$ because at lower temperature the rate constants of atom excitation and ionization are negligible. From this it follows also that the analysis of the ionization balance is necessary also to describe a certain gas discharge plasma. Fig. 4 gives the dependence of the electron temperature on the reduced electric field strength for heavy inert gases. This Figure shows a range of reduced electric field strengths at which a stable gas discharge plasma exists. We give also in Fig. 5 the dependencies on the electron temperature T_e for the rate constant of atom excitation by electron impact in a gas discharge plasma in accordance with formula.

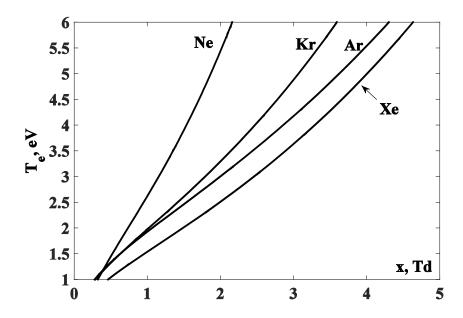


Figure 4: Electron temperature as a function of the reduced electric field strength in the regime of a high electron concentration.

It should be noted that though according to the criterion exchange by energy in electron-atom collisions is less compared with that in electron-atom collisions, electron-atom collisions are of importance for a change of the electron energy because electron-electron collisions do not lead to variation an average energy of the electron subsystem. Moreover, the electron temperature is determined by electron-atom collisions in the case. Indeed, the power which is transferred to one electron from an external field is eEw_e , where w_e is the electron drift velocity in a gas under the action of an external electric field of a strength E, and electrons gives an energy to a gas as a result of electron-atom collision. Correspondingly, we have the following balance equation

$$eEw_e \sim \frac{m_e}{M} v_{ea} (T_e - T), \tag{2.38}$$

where M is the atom mass, and T is the gas temperature. In particular, if $T_e >> T$, we have $T_e \sim M w_e^2$, and this situation is supported by a small parameter m_e / M . One can give precise expressions for the electron drift velocity w_e and the difference between the electron T_e and gas temperature T (for example, [37, 17])

$$w_e = \frac{eE}{3T_e} \left\langle \frac{v^2}{v_{ea}} \right\rangle, T_e - T = \frac{Ma^2}{3} \frac{\left\langle v^2 / nu_{ea} \right\rangle}{v^2 v_{ea}}$$
(2.39)

These estimations correspond to estimation.

Processes under consideration lead to gas heating, and the heat balance equation has the form

$$\frac{3}{2}N_a \frac{dT}{dt} = N_e e E w_e, \tag{2.40}$$

if we neglect the heat release. As is seen, the slowness of gas heating results from a small electron concentration in a gas discharge plasma. As is seen, a stationary state of a gas discharge plasma requires the analysis of the heat balance equation.

Thus, an effort to describe a certain gas discharge plasma, where along elastic electron -atom and electronelectron collisions processes of excitation of atoms in the ground state and quenching of excited atoms are of importance, on the basis of the kinetic equation for electrons, is not precise in principle. It is necessary to add the kinetic equation for electrons by equations of the ionization balance and heat balance. Hence, along with cross section of elastic and inelastic electron-atom collisions, a description of a gas discharge plasma must be based also on additional information.

3. TRANSFER PROCESSES IN GAS DISCHARGE PLASMA INVOLVING EXCITED ATOMS

3.1 Quenching of Excited Atoms in Gas Discharge Plasma

We above convince that it is necessary for the total description of a certain gas discharge plasma along with the kinetic equation for the EEDF to use equations of the ionization and heat balance [2]. Moreover, heat transfer leads to a plasma nonuniformity because it is determined by temperature gradients. In particular, in a widespread case of a gas discharge plasma of the positive column of gas discharge in a cylinder tube this leads to the dependence of the gas temperature T on a distance from the tube axis. This fact may be of importance for other plasma parameters at not low discharge powers. Nevertheless, in the case of a fast establishment of the electron equilibrium between ground and excited atom states, one can use this equilibrium locally using the electron temperature or an analogous energetic parameter of the EEDF as a phenomenological parameter. Basing on this approach, we below find the concentration of excited atoms, restricting ourselves by the regime of a high electron concentration where the electron temperature T_e may be used as a characteristic of the EEDF.

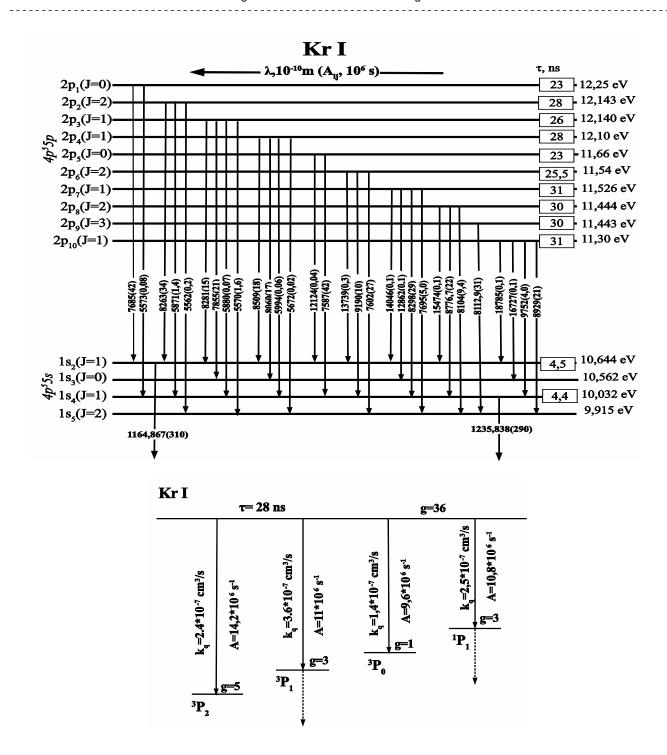


Figure 5: Transition from a general case with using the partial rates of radiative transitions from states of the electron shell $Kr(4p^5p)$ of the krypton atom to the states of the electron shell $Kr(4p^5s)$ to the rates averaged over the group of states with the electron shell $Kr(4p^5p)$. The transition energies are expressed in eV, g, is the statistical weight of the corresponding level, and the rates of radiative transitions are given in 10^6s^{-1} near an indicated arrow.

We above assume that the EEDF falls sharply near the atom excitation threshold. This means that the rate constant of quenching is large compared with this process with transition in the ground state. The ground state of inert gas atoms is np^{6} $^{1}S_{0}$, where n is the principal number of a valence electrons, and the electron shell for the group

of the lowest excited states is np^5 (n+1)s. There are 4 states of this group (see Table 2), and we use for them notations of the LS-coupling, according to each these states are 3P_2 , 3P_1 , 3P_0 , 1P_1 , in the order of an increase of the excitation energy. Quenching of these states results mostly as a result of transitions into the group of states with the electron shell np^5 (n+1)p. There are 10 such states Let us denote the rate constants for transitions from a given state of the group np^5 (n+1)p in states of the group n

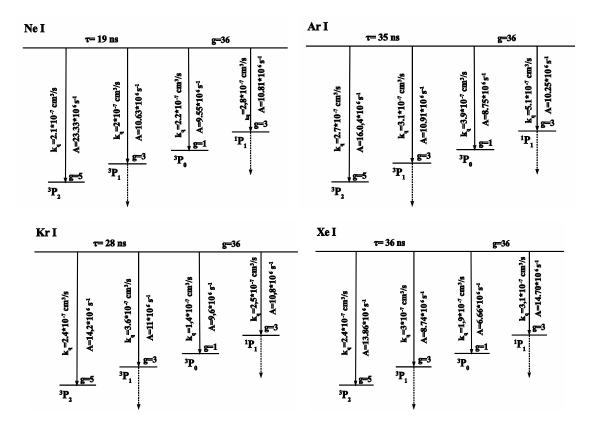


Figure 6: Quenching rate constants in electron-atom collisions for transitions from states of the electron shell np^5 (n+1)p to states of the electron shell np^5 (n+1)s. Quenching rate constants rates are averaged overupper states states and correspond to one electron state of a lower level. The indicated rate constants correspond to neon, argon, krypton and xenon atoms.

The excitation average energy of a transition E_i into a given state of the lower group is defined as

$$E_{i} = \frac{\sum_{j} g_{j} E_{ij}}{\sum_{j} g_{j}}, \sum_{j} g_{j} = 36$$
(3.1)

where indices i and j correspond to the lower and upper transition states, and an average is made over the group of upper states. Correspondingly, the radiative rates $1/\tau_i$ averaged over upper states into states i is given by

$$\frac{1}{\tau_i} = \frac{\sum_j g_j / \tau_{ji}}{\sum_j g_j} \tag{3.2}$$

One can compare the rates per one lower levels $1/(g_i \tau_i)$, and their dispesion testifies about the accuracy of the block method. We find also the average excitation energy as

$$\Delta \varepsilon = \frac{\sum_{i} g_{j} E_{i}}{\sum_{i} g_{i}}, \sum_{i} g_{i} = 12$$
(3.3)

In the same manner one can determine the radiative transition rates averaged over the state group with the electron shell $p^5(n+1)$. One can define the average rate of radiative transition between states of indicated groups as

$$\frac{1}{\tau_r} = \frac{\sum_i g_i / \tau_i}{\sum_i g_i} \tag{3.4}$$

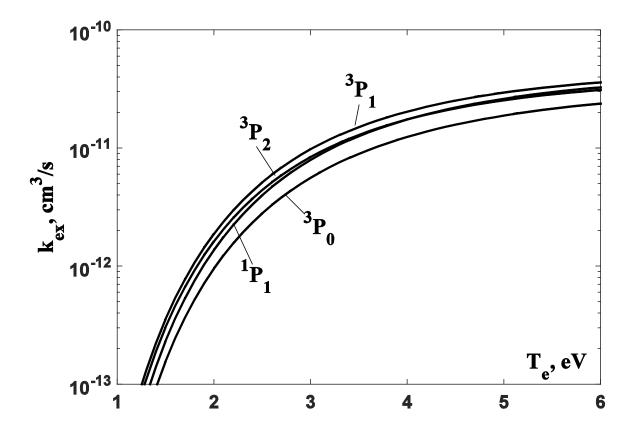


Figure 7: Partial rate constants for transitions from states of the electron shell Kr ($4p^5s$) to states of the electron shell Kr ($4p^5p$) in collisions with electrons. The transition rates are averaged over the final states.

Table 3
Parameters of transitions from states of the group np^5 (n+1)p in the states of the group np^5 (n+1)s for inert gas atoms

Atom	Ne	Ar	Kr	Xe
$\Delta \varepsilon$, eV	2.1	1.65	1.6	1.5
$1/\tau_r, s^{-1}$	15.87	12.4	12	12.1
k_q , $10^{-7} sm^3 / s$	2.3	3.52	2.6	2.68

Table 3 contains average parameters of transitions from states of the group $np^5(n+1)p$ in the states of the group $np^5(n+1)s$ for inert gas atoms, namely, $\Delta \varepsilon$, $1/tau_p,k_q$. The rate constant of the inverse transition k_Q follows from the principle of detailed equilibrium. Fig. 6 contains the electron temperature dependence for the rates of transition from states of the lower group of excited states with the electron shell $np^5(n+1)s$ to states with the electron shell $np^5(n+1)p$ as a result of collisions with electrons. It should be note that the quenching rate constants are normalized to one state of the lower state group. Correspondingly, defining k_Q as the sum of the rate constants for transitions from one state of the lower group $np^5(n+1)s$ to states of the upper group of states with the electron shell $np^5(n+1)p$, we obtain the following expression for the transition rate on the basis of the principle of detailed balance

$$k_{\mathcal{Q}} = 3k_q \exp\left(-\frac{\Delta E}{T_e}\right),\tag{3.5}$$

where ΔE is the transition energy, T_e is the electron temperature.

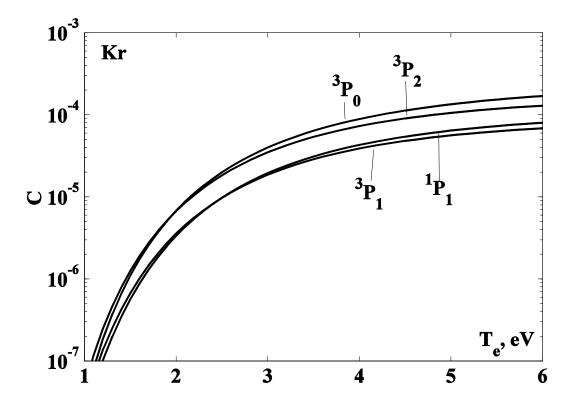


Figure 8: Concentrations of krypton atoms in excited states which belong to the electron shell $Kr(4p^5s)$ as a function of the electron temperature.

Comparing the rate constants of Fig. 7 with the rate constants of quenching of the lowest excited states of inert gas atoms by electron impact given in Table 2, one can conclude that quenching of these states results from excitation in upper atom states in a range of electron temperatures under consideration. On the basis of the above rate constants one can find the concentration of excited atoms which are given by formula

$$c_i = \frac{k_{ex}}{k_{Oi}},\tag{3.6}$$

where the excitation rate constant k_{ex} is determined by formula, and we assume that decay of these states results from transition in states of the shell $Kr(4p^5p)$, as it follows from estimations. Indeed, the electron shell $Kr(4p^5s)$ is connected with the electron shell $Kr(4p^5p)$ by dipole radiative transitions, and therefore transitions between these states are effective. In addition, the transitions energies open these transitions for electron energies where ionization from excited states is effective. Fig. 7 contains the concentration of excited krypton atoms in excited states of the lowest state group with the electron shell $Kr(4p^5s)$. We assume the electron number density N_e in a gas discharge plasma satisfies to the criterion

$$N_e \gg \frac{1}{k_q \tau_r},\tag{3.7}$$

i.e. radiative transitions from the upper states do not influence on the character of decay.

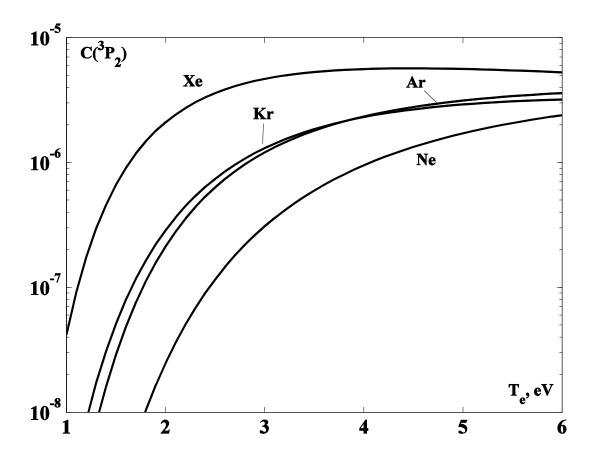


Figure 9: Concentrations of inert gas atoms in the lowest excited state ${}^{3}P_{2}$ as a function of the electron temperature.

3.2 Mixing of Lower Excited States of Inert Gas Atoms in Plasma

In analyzing the processes in a gas discharge plasma with participation of excited atoms we restrict ourselves by transitions between excited states which are coupled by radiative dipole transitions because it is a strong interaction. Therefore in the above consideration we assume states of the lower group with the electron shell np^5 (n+1)s to be not mixed. From the other standpoint, the energy difference for states of a given group is relatively small, and hence transitions between these states may be effective in spite of a weaker interaction. In particular, the exchange mechanism of state mixing proceeds as a result of exchange between incident and valence electrons in electron-atom collisions according to the scheme [43, 3]

$$e \downarrow + A(np^5(n+1)s \uparrow) \rightarrow e \uparrow + A(np^5(n+1)s \downarrow),$$
 (3.8)

where \$e\$e is an incident electron, \$A\$A is an inert gas atom, the arrow indicates the electron spin direction. The rate constants of these transitions may be found on the basis of the experimental scheme by Phelps [45]. In particular, in the case of neon we have for the rates of transitions between states of the group $\$Ne(2p^53p)\$$ according to measurements [44]

$$e + Ne(2p^{5}3s^{3}P_{1}) \rightarrow e + Ne(2p^{5}3s^{3}P_{2}), k = 1.25 \cdot 10^{-7} cm^{3} / s,$$

$$e + Ne(2p^{5}3s^{3}P_{0}) \rightarrow e + Ne(2p^{5}3s^{3}P_{2}), k = 1.7 \cdot 10^{-8} cm^{3} / s,$$

$$e + Ne(2p^{5}3s^{3}P_{0}) \rightarrow e + Ne(2p^{5}3s^{3}P_{1}), k = 4.4 \cdot 10^{-8} cm^{3} / s,$$

$$(3.9)$$

We do not indicate the accuracy of given results of measurements [44] because we use them for conclusions.

Comparing the rate constants of level mixing by electron impact with the rate constants of transitions in states of an upper shell given in Fig. 7 one can conclude that under these conditions mixing between states of the group np^5 (n+1)s of lowest excited states of inert gas atoms in collisions with electrons is weak compared to transition in states of the upper state group, if the electron temperature exceeds 1 eV.

Another mechanism of transitions between states of the group np^5 (n+1)s results in collisions with atoms in the ground state [45]. Though the rate constants of such processes are relatively small, their rates may be not small because of a large number density of atoms compared to electrons, especially at high electron number densities. Hence, though we ignore the processes of mixing of one group states, they must be taken into account under certain conditions.

3.3 Emission of Excited Atoms in Gas Discharge Plasma

As it follows from the above analysis, effective processes of transition between atom states as a result of collisions with electrons proceed between states with a dipole coupling, i.e. if the matrix element of the dipole moment operator is not zero for these transitions. But then effective radiative transitions take place between these states. Therefore quenching of excited states of these transitions is possible due to radiative transitions, and if the ground atom state is the lower state of these transitions, radiation is locked in this gas discharge plasma. As a result, the effective lifetime of the upper atom state in a gas discharge plasma is higher by orders of magnitude compared with that of an isolated atom due to reabsorption processes. We below briefly consider this problem [43, 3].

The efficiency of reabsorption process is determined by broadening of spectral lines, and for the resonant excited atom the width of a spectral line v is connected with the total cross section of collisions of atoms in the ground and resonantly excited states σ_t by formula [46]

$$v = \frac{1}{2} \langle N_a v \sigma_t \rangle, \tag{3.10}$$

We below assume the Lorentz form of spectral line, as it takes place usually for used gas pressures of a gas discharge plasma, and because reabsorption process for resonant radiation is significant, the following criterion holds true for the absorption k_a coefficient at the line center

$$k_{o}R \gg 1 \tag{3.11}$$

where R is a typical size of a gas discharge plasma (A radius of the discharge tube if this plasma is a positive column of gas discharge).

 $Kr(^{1}P_{1})$ $Xe(^{3}P_{1})$ $Ne(^{3}P_{1})$ $Ne(^{1}P_{1})$ $Ar(^{3}P_{1})$ $Ar(^{1}P_{1})$ $Kr(^3P_1)$ $Xe(^{1}P_{1})$ Atom 743.719 735.896 1066.6 1048.22 1235.838 1164.867 1469.61 1295.586 λ,A 2 25 1.6 10 4.4 4.5 3.6 3.5 τ_{ν} ,ns 3 45 2.9 15 6 6.4 4.6 4.7 τ_{eff} , μs

Table 4
Parameters of resonantly excited atoms

Note that the in this case of collisions of atoms whose states differ by electron transfer between s and p states the processes of elastic scattering of atoms, excitation transfer and depolarization of a p electron in the course of atom collisions are entangled. The partial and total cross section of this process were evaluated in [57, 47], and and we use below the results of indicated numerical evaluations which relate to the s-p transition only. Estimations may lead to an error, as it takes in paper [54]) where the total cross section was taken in seven times lower.

Thus, we use below the Veklenko theory [48] for reabsorption of radiative radiation. As a result of the reabsorption process, the effective lifetime τ_{ef} of resonantly excited atoms increases compared with the radiative lifetime τ_r of an isolated atom. In particular, if a uniform gas discharge plasma is located inside a cylinder tube of a radius \$R\$R, the effective lifetime of a resonantly excited atoms inside this plasma is equal [3]

$$\tau_{ef} = 4.9\tau \sqrt{\frac{R}{\lambda}},\tag{3.12}$$

where λ is the wavelength of resonant radiation. We give in Table 4 the effective radiative for resonantly excited atoms of inert gas atoms whose states belong to the lowest group with the electron shell $np^5(n+1)s$.

In addition, the reabsorption process is of importance for kinetics of resonantly excited states. In particular, the concentration of atoms in this state is given by

$$c_i = \frac{k_{ex}}{\left[k_{Qi} + 1(N_e \tau_i)\right]} \tag{3.13}$$

instead of formula. Here τ_i is the effective radiative lifetime of this resonantly excited state. In Fig.9 we use the number density of electrons $N_e = 10^{12} \ cm^{-3}$.

3.4 Stepwise Ionization in Gas Discharge Plasma

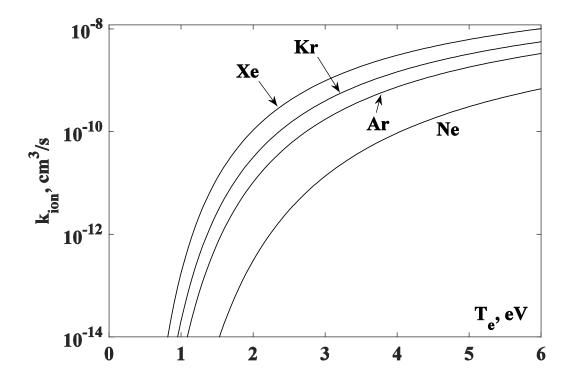


Figure 10: Rates of stepwise ionization involving excited atoms of inert gases of the group states with the electron shell $np^5(n+1)s$.

In considering stepwise ionization of inert gas atoms by electron impact in a gas discharge plasma, we assume that ionization is created by excited atoms of the group with the electron shell

 $np^5(n+1)s$. Taking the Maxwell distribution function of electrons $f(\varepsilon)$, we use the rate constant of atom ionization based on the experimental data for ionization of a valence s-electron that is given by [3]

$$k_{ion} = \int \sqrt{\frac{2\varepsilon}{\pi m_e}} \frac{2}{\sqrt{\pi} T_e^{3/2}} \sqrt{\varepsilon} \exp\left(-\frac{\varepsilon}{T_e}\right) d\varepsilon \frac{\pi e^4}{J^2} f(x)$$
 (3.14)

Assuming the electron temperature T_E to be small compared to the atom ionization potential J (the temperature is expressed in energetic units), we have for the rate of ionization for an atom in a given excited state where an excited electron is found in s-state [3]

$$k_{ion} = 10\sqrt{\frac{8\pi T_e}{m_e}} \frac{e^4}{J^2} \exp(-J/T_e) \cdot (9 + T_e/J)^{-1}$$
(3.15)

If the rate constant is expressed in cm^3/s and the electron temperature T_e , as well the atom ionization potential \$J\$J, are expressed in \$eV\$eV, the ionization rate constant is given by [3]

$$k_{ion}(T_e) = 4.85 \cdot 10^{-6} \frac{\sqrt{T_e}}{J^2 [1 + T_e / (9J)]} \exp\left(-\frac{J}{T_e}\right)$$
 (3.16)

From this it follows for the rate constant of stepwise ionization as a sum of partial rate constants over states as

$$k_{ion}(T_e) = \sum_{i} c_i k_{ion}^i,$$
 (3.17)

where c_i is the concentration of excited atoms in *i*-th excited state of the group with the electron shell $np^5(n+1)s$, K_{ion}^i is the rate constant of ionization from an excited state *i*. It should be noted that the rate of ionization of atoms by electron impact in this case is given by

$$\frac{dN_e}{dt} = N_a k_{ion}(T_e),\tag{3.18}$$

where N_a is the number density of atoms in the ground state.

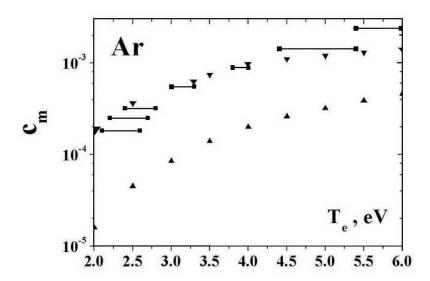


Figure 11: Concentration of metastable argon atoms $Ar(^3P_2)$ as a function of the electron temperature. Triangles correspond to formula, upturned triangles relate to low electron number densities where quenching of excited atoms is determined by atom ionization, and signs relate to experimental data [56]

In this scheme we ignore radiative transitions from excited states. Let us analyze the situation which is realized in an inductive gas discharge plasma where the number density of electrons is relatively small. Then radiative transitions from the states of the electron shell $np^5(n+1)p$ of inert gas atoms in states with the electron shell $np^5(n+1)s$ increase the concentration of metastable states of the lower group with an increasing number density of electrons. Moreover, in the limit of relatively small electron number densities ionization processes become responsible for decay of metastable states, and the concentration of metastable atoms is given by formula

$$c_i = \frac{k_{ex}}{k_{ion}},\tag{3.19}$$

instead of formula. As demonstration of this, the concentrations of metastable argon atoms of argon gas discharge plasma are compared in Fig. 11 for cases where quenching of metastable states result from transitions in the next electron shell and is determined by atom ionization. The latter is chosen by experimental data [56].

4. CONCLUSION

This paper is devoted to theoretical analysis of a stationary gas discharge plasma of inert gases with stepwise ionization, where excited atoms influences on the plasma behavior. In this analysis we keep a general scheme of kinetic of electrons and excited atoms (for example, [49, 50, 51, 52, 53, 54]). In this scheme along with the kinetic equation for the electron distribution function by energy, the balance equations for number densities of excited atoms are included in consideration. The cross sections of electron-atom collisions play the principal role in this scheme. As it was indicated above, the theory is not releable in this because can not take into account exchange interactions between incident and valence electrons, whereas experimental information is scare. We use here the scaling law for cross sections of transitions between s and p states of valence electrons as a result of electron impact. This allows us to determine the rates of these transitions on the basis of experimental data for alkali metal atoms. From this we obtain the concentrations of excited atoms in a gas discharge plasma of inert gases and the rate constant of stepwise ionization that is the basis of the analysis of other properties of this gas discharge plasma. Unfortunately, we have not explanation in indicated vapor which cross section were used there as if it is a routine problem.

As a result of this analysis, we found that only lower excited states of inert gas atoms of groups with electron shells $np^5(n+1)s$ and $np^5(n+1)p$ may be responsible for stepwise ionization, and only these states may be taken into account. Note that in the Vlacek model [50] which is the basis of papers [51, 52, 53] 64 levels are included in consideration. But using states which do not give the contribution to ionization processes does not improve the reliability of numerical calculations.

The self-consistent character of atom excitation in a gas discharge plasma [4, 5, 37] is of importance in this scheme. Unfortunately, this fact is not taken into account in indicated papers. Indeed, due to sharp drop of the EEDF with increasing energy of an incident electron, as it is shown in Fig.1, excited states of other groups can not be resulted from electron collisions with an atom in the ground state, and excited atoms with higher excitation energies may be formed in collisions of plasma electrons with excited atoms in lower states. As a result, population of atoms in higher excited states is lower compared with that in states of the group $np^5(n+1)s$. According to results of indicated papers, the populations of excited levels, where they are given, are compared for states the group $np^5(n+1)s$ and higher excited levels. This testifies that the self-consistence of the atom excitation process in collisions with electrons is not fulfill in these calculations.

To sum up for this analysis, we mark the complexity of kinetics of a gas discharge plasma because of a large number of processes which are responsible for the behavior of this plasma and due a large number of regimes of this plasma. Therefore, construction of a universal scheme for plasma kinetics is not productive for a gas discharge plasma where processes with participation of excited atoms are of importance. In this way one can join some regimes of a gas discharge plasma of a certain type with identical processes and properties under consideration. It is of importance in this way to ground the cross sections and rate constants of processes used.

Acknowledgement

The study was supported by Russian Science Foundation (grant No. 14-50-00124)

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